ORIGINAL PAPER

Effect of Temperature and Oxygen on Luminescence Spectra and Polarization of Divinylbenzoxazolylbiphenyl Thin Films

A. V. Kukhta · E. E Kolesnik · I. N. Kukhta ·
E. V. Dudko · V. A. Tolkachev · K. A. Osipov ·
V. N. Pavlovskii · V. K. Olkhovik · N. A. Galinovskii

Abstract H-type molecular aggregation as assembly with chromophore dipoles arranged parallel to each other has been observed in absorption and luminescence spectra of divinylbenzoxazolylbiphenyl thin films deposited on quartz glass substrate by thermovacuum method. The reversible changes of fluorescence anisotropy have been observed under film heating below the glass transition temperature correlating with lifetime changes. The addition of oxygen was found to cause an essential luminescence quenching. The hexyloxy group in the side chain of dibenzoxazolylbiphenyl molecule decreases H-type molecular aggregation and energy migration, and increases luminescence quenching induced by adsorbed oxygen owing to the formation of more porous film morphology.

Keywords Divinylbenzoxazolylbiphenyl · Thin film · Luminescence · Polarization · Quenching · Temperature · Oxygen

A. V. Kukhta (✉) · E. E Kolesnik · I. N. Kukhta · E. V. Dudko ·
V. A. Tolkachev · K. A. Osipov · V. N. Pavlovskii
B.I. Stepanov Institute of Physics of the National
Academy of Sciences of Belarus,
Nezalezhnastsi Ave. 68,
220072 Minsk, Belarus
e-mail: Kukhta@imaph.bas-net.by

V. K. Olkhovik · N. A. Galinovskii
Institute of Chemistry of New Materials of the National
Academy of Sciences of Belarus,
F. Skaryny Str. 36,
220141 Minsk, Belarus

Introduction

Organic thin films have attracted wide attention not only for versatile properties but also for manifold technological applications, such as field effect transistors, photovoltaic cells, electroluminescence diodes, etc. [1]. Among various organic materials, π-conjugated organic molecules are the most interesting due to their peculiar electronic properties. With these materials thin glasslike films can be prepared by different methods in particular by thermo vacuum deposition. The morphology of obtained films determines essentially both optical and electronic properties. As a rule, such films are formed amorphous. But, it was shown [2] that the type of the molecule, nature and temperature of the substrate, the deposition rate and film thickness determine molecular orientation in the film resulting in strong effect on absorption and luminescence behavior of the molecules and charge carriers mobility [3, 4]. In the real device the morphology of organic film can be changed owing to the temperature increase caused by Joule heating during the device operation, as well as the action of oxygen adsorbed by a film after deposition. The concentration of adsorbed oxygen is known to depend on the temperature value [5]. The high efficiency of oxygen quenching of singlet excited states in aromatic and heteroaromatic compounds strongly correlates with a high reactivity of molecules with oxygen [6]. These two factors determine the durability and performance characteristics of organic film based electronic devices [7].

In this paper, the action of temperature and oxygen addition on absorption and luminescence for thin films of two derivatives of divinylbenzoxazolylbiphenyl has been studied by the method of polarized luminescence. Such compounds are known as laser dyes as well as emitting and charge transporting materials for molecular electronic devices [8]. They can also serve as some model approach

compounds of electroactive polymer like polyphenylenevinylene and its derivatives. Polarized luminescence spectroscopy has been used extensively to study molecular orientational characteristics of anisotropic samples such as liquid crystalline materials, stretched polymers, and adsorbed dyes [9, 10].

Experimental

The measurements of polarized luminescence anisotropy were made in the standard excitation–observation orthogonal scheme, using a set-up described earlier [11]. The xenon high pressure arc lamp with a power of 1,000 W served as a source of excitation. 300 Hz modulated exciting light beam was transmitted through a monochromator and additional absorption filters to remove the scattered light with other wavelengths, and then through polarizing Glan prism. The sample surface has been situated at an angle of 45° relative to the excitation light beam. Fluorescence passed through an analyzing polarizer was registered by a photomultiplier placed orthogonally to the sample surface. Both excitation intensity reference signal and integral fluorescence anisotropy signal entered lock-in amplifier and then amplitude digital converter connected to computer. An absolute error of polarization degree measurements did not exceed 1%. The absolute value of anisotropy r are determined using standard relation $r = (I_{II} - I_{\perp})/(I_{II} + 2I_{\perp})$, where I_{II} and $I_{\perp}$ are the intensities of parallel and perpendicular to exciting beam polarization components correspondingly. The sample was placed in a fused silica cell under vacuum of about 10^{-4} Torr or in air. The concentration of adsorbed oxygen is known to decrease during heating. The minimal oxygen concentration in the sample was determined by both its temperature and vacuum degree, the maximal value reached 510 Torr added from the external source. The films were obtained by thermo vacuum deposition on a precleaned fused silica substrate at room temperature under vacuum of about 10^{-6} Torr. The surface of the substrate is amorphous and inert. The deposition rate was less than 0.1 nm/s. The thickness of the films varied from 30 to 150 nm. The quartz microbalance method is used for thickness measurements at the first deposition; then the thickness has been determined by optical absorption method. The chemical structures of studied compounds are presented in Fig. 1. The synthesis of these compounds is described in [12]. After synthesis both sample powders were purified by sublimation. 4,4'-Bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl) 2-n-hexyloxy]biphenyl (DBBHO) differs from 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]biphenyl (DBB) by the presence of a side aliphatic chain. As a rule, the introduction of extensional side substituents into the main molecule polyphenylenevinylene chain results in

an increase of solubility and a decrease the thin film crystallization [13]. The film properties are monitored through light intensity and anisotropy during the heating and oxygen addition. Optical absorption and luminescence spectra were recorded using a spectrophotometer Cary 500 Scan ultraviolet–visible–near-infrared (Varian) and a fluorometer SFL-1211A (Solar TII), respectively.

Results and discussion

The freshly prepared films of both compounds were smooth and transparent. After some period the DBBHO film clearly became lusterless and much less transparent. The absorption and luminescence spectra of solutions and thin films for both compounds are presented in Fig. 2. No reabsorption and interference effects have been observed in the spectra using film thicknesses from 30 to 150 nm. The absorption spectra of both compounds in toluene solution display a symmetrical intense band near 375 nm due to the isolated chromophores i.e. under conditions of weak intermolecular interaction. The absorption spectrum of DBB film is rather unusual. It is blue shifted ($\lambda_{max}=$ 320 nm) and the shape of spectrum is highly skewer than that of solution ($\lambda_{max}=373$ nm) exhibiting nearly symmetric band. An unusual vibronic structure at 430 nm is also observed. The similar behaviour was observed earlier for liquid crystalline polymers with a side chain [14] and for linear π-conjugated molecules [15]. The observed left-skewed shape of spectrum can be explained by at least two kinds of π–π* electronic transitions in the studied film [14]. One is the transition in H-aggregated chromophores ($\lambda_{max}\sim$ 320 nm) with parallel dipole–dipole arrangement and the other is in isolated chromophores ($\lambda_{max}\sim370$ nm). The conditions of such behaviour for molecules of DBB are much better than for above mentioned liquid crystalline
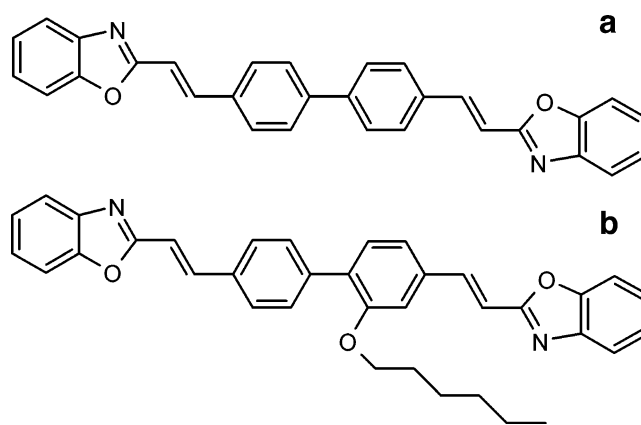
Fig. 1 Molecular structures of substances under study. **a** Compound 1: 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]biphenyl (DBB); **b** Compound 2: 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl) 2-n-hexyloxy]biphenyl (DBBHO)
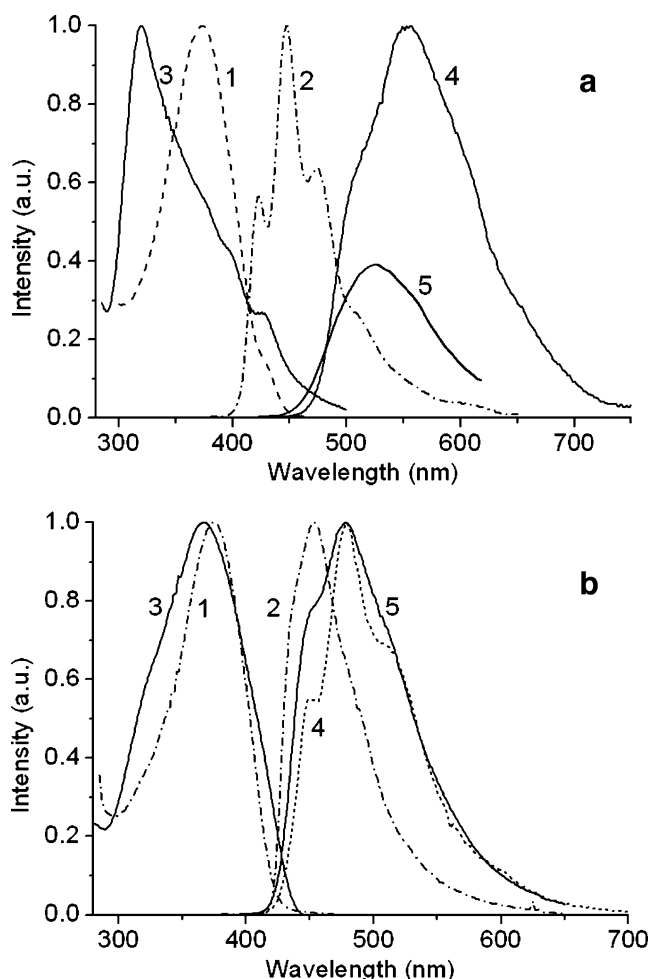
Fig. 2 Absorption (*1, 3*) and luminescence (*2, 4, 5*) spectra of solutions (*1, 2*) and thin films (*3, 4, 5*) for DBB (**a**) and DBBHO (**b**); **a** film heated to 100 °C (*5*); **b** fresh (*5*) and old film (*4*)

polymers. During the storage time (several days) this spectrum does not reveal visible changes. As a rule, luminescent molecules in ordered solid-state structures tend to have π–π interactions among the planar π-conjugated backbones, which lead to the formation of molecular aggregates and often result in red-shifted luminescence spectra [16]. The excitation spectra differ from absorption spectra for the film DBB. They are not left-skewed and are closer to absorption spectrum of solution though with a feature in a short-wavelength shoulder. After the heating the intensity of these spectra decreases. The luminescence spectrum of compound 1 film is strongly red shifted and broadened as well as structureless as compared to solution spectrum having a vibrational structure. It has a maximum at 560 nm and a feature at 500 nm which can apparently be ascribed to aggregate and monomer emission correspondingly. Such behaviour reflects strong intermolecular interactions. The gradual heating of this film up to 100 °C (that is below the glass transition) results in the luminescence intensity decrease (see curve 5 in Fig. 2a). No threshold

behaviour has been observed under measuring through every 10 °C. The shape of this spectrum is also changed. The longwave part of the spectrum decreases, and luminescence maximum moves to shorter wavelengths. The gradual cooling of the sample results in opposite reversible spectrum transformations. The luminescence spectra measured at two excitation wavelengths, at the beginning and at the end of longwave absorption band, are fully coincided, as well as temperature changes. The ratio in luminescence intensities measured for two excitation wavelengths approximately corresponds to absorbances (the ratio of absorbances is only 14% higher than the ratio of luminescence intensities). The kinetics of the fluorescence decay is double-exponential for both monomer (2 and 12.8 ns) and aggregate (3.4 and 13.5 ns) spectrum parts. The heating of the sample 1 from room temperature to 100 °C results in the 2 and 3.7 times decrease of the fast component in fluorescence decay time for monomer and aggregate emission correspondingly. The decrease of the slow component is 2.6 times for both cases. Such behaviour can be explained by enhancing of intermolecular non-radiative transitions as well as by changing of proportions of aggregated and free molecules in the formation of luminescence spectrum i.e. by transformation of luminescence sites. The heating above the temperature of glass transition can result in irreversible changes. The irradiation of this film by partially polarized nitrogen laser (337 nm, 250 kW/cm^2) also resulted in the slight luminescence intensity decrease up to about 10% in 12 min but no spectrum shape changes have been observed.

The absorption spectra for DBBHO in solutions and thin films are rather similar (see Fig. 2b). Thin film spectra are slightly broadened and slightly blue shifted. A little hypsochromic shift of absorption longwave maximum has been also observed in spin deposited polyethylhexyloxy-phenylenevinylene film as compared to its solution spectrum [17]. The fluorescence spectrum of DBBHO in solution is structureless as well as intermolecular interactions are lower owing to steric hindrance by hexyloxy group. The spectrum of the film is broadened and has signs of vibrational structure. After some time this spectrum becomes more structural and film morphology is changed from amorphous to branched herringbone polycrystalline with dimensions up to 4.5 μm long [12].

Figure 3 illustrates temperature changes of relative anisotropy for both compounds in vacuum and with 510 Torr oxygen. The measurements are made below the glass transition temperature (far below for DBB). After the film heating from 20 to 100 °C the 45% and 17% approximately linear increase of fluorescence anisotropy for DBB and DBBHO correspondingly is observed. The reproducible value of polarization degree for DBB at room temperature is about 17% and slightly depends on the film angle relative
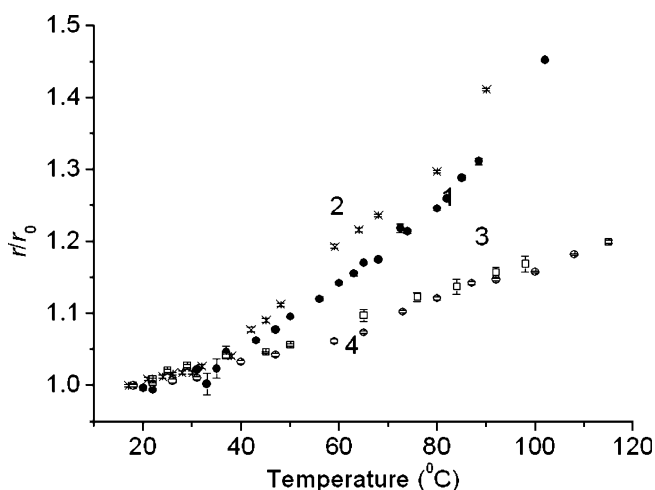
Fig. 3 Temperature changes of relative anisotropy for DBB (*1*, *2*) and DBBHO (*3*, *4*) in vacuum (*1*, *3*) and with 510 Torr oxygen (*2*, *4*). Excitation wavelength is 390 nm, registration wavelength is integral over the whole spectrum

to excitation light electrical vector. The presence of air or oxygen did not change essentially these curves. It is interesting that the observed changes of anisotropy are reversible. Fourfold process of the temperature increase and decrease showed the same anisotropy dependence both in air and vacuum. The increase of fluorescence anisotropy can be explained by changing of the fluorescence quantum yield due to a lifetime decrease caused by enhanced nonradiative deactivation, and the formation of some partly ordered structure of excited molecules. With an increase of the temperature, the mobility of the molecule parts for angular motion and stabilization increases, leading to a high and stable value of the luminescence anisotropy. The strongly coupled chromophores in the aggregates are likely to induce higher luminescence anisotropy than the free chromophores at irradiation by the linearly polarized pump beam. But, the process of molecule rearrangement is rather slow, it takes some minutes for liquid crystalline polymer [9]. Moreover, an atomic force microscopy did not reveal any morphology changes with temperature except slight surface smoothing. On the other hand, the observed decreasing of fluorescence lifetime causes always an anisotropy enhancement in accordance with orientation diffusion Perrin's formula $r = r_0/(1 + \tau/\rho)$, where ρ is the coefficient and τ is the fluorescence lifetime after heating. Then the averaged value of the anisotropy increase is 38% that is rather close to experimental value at 100 °C (see Fig. 2). The growth of nonradiative transitions during the heating is known to connect with energy migration. Thus, the less increase of anisotropy for DBBHO can also be connected with the presence of steric hindrance hampering the process of energy migration.

The dependence of luminescence quenching at oxygen addition and its linear approximation are presented in

Fig. 4. The quenching value is determined as a ratio between initial luminescence intensity and luminescence observed at oxygen addition. For DBB the observed luminescence quenching is negligible. DBBHO reveals more essential quenching apparently also due to the presence of steric hindrance. Actually, the additional side group does not contribute to molecular π-electron system and absorption coefficient. It is known [13] that hexyloxy substituents in the side position result in the increase of the rotation angle between biphenyl parts. The presence of this group initiates the formation of more porous film morphology, and oxygen molecules can easier penetrate into the film causing luminescence quenching. More effective oxygen adsorption can be the possible reason of much less photostability of DBBHO film as compared to DBB [12].

Conclusion

The effect of temperature and oxygen on luminescence spectra, intensity and anisotropy of divinylbenzoxazolylbiphenyl thin films thermovacuum deposited on fused silica substrate has been studied. H-type molecular aggregation with chromophores dipoles arranged parallel to each other has been observed in absorption and luminescence spectra. The reversible changes of fluorescence anisotropy have been observed under film heating below the glass transition temperature correlating with lifetime changes. The addition of oxygen was found to cause an essential luminescence quenching. The hexyloxy group in the side chain of this molecule decreases H-type molecular aggregation and energy migration, and increases adsorbed oxygen induced luminescence quenching apparently owing to the formation of more porous film morphology. Divinylbenzoxazolylbiphenyl without side groups forms highly stable and luminescent thin films owing to strong H-type molecular
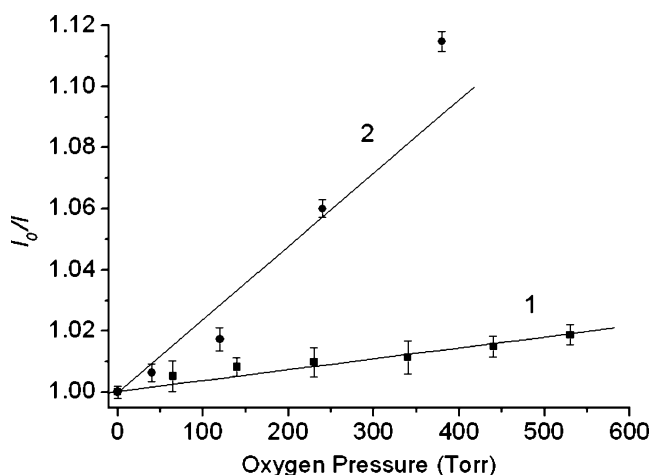
Fig. 4. Fluorescence quenching by oxygen addition for DBB (*1*) and DBBHO (*2*)

aggregation. These properties as well as low oxygen quenching allow to conclude the prospects of these substances for molecular electronics devices, in particular for electroluminescent diodes [18].

References

1. Kukhta AV (2003) Electroluminescence of thin films of organic compounds. J Appl Spectrosc 70:165–194
2. Leising G, Tasch S, Graupner W (1997) In: Skothem T, Elsenbaumer R, Reynolds J (eds) Handbook of conducting polymers. Marcel Dekker, New York, pp 847–880
3. Dholakia GR, Fan W, Koehne J, Han J, Meyyappan M (2004) Transport in self-assembled molecular wires: effect of packing and order. Phys Rev B 69:153402
4. Kukhta AV (2005) Transport of low-energy electrons in thin organic films. Mol Cryst Liq Cryst 427:71–93
5. Kukhta AV, Kolesnik EE, Lappo AN, Pochtennyi AE, Grabchev IK (2004) Electrophysical and luminescent properties of PAMAM dendrimers based on naphthalimide moieties. Phys Solid State 46:2229–2232
6. Aubry J-M, Pierlot C, Rigaudy J, Schmidt R (2003) Reversible binding of oxygen to aromatic compounds. Acc Chem Res 36 (9):668–675
7. Tokito S, Tanaka H, Okada A, Taga Y (1996) High-temperature operation of an electroluminescent device fabricated using a novel triphenylamine derivative. Appl Phys Lett 69(7):878–880
8. Hosokawa C, Higashi H, Nakamura H, Kusumoto T (1995) Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant. Appl Phys Lett 67(26):3853–3855
9. Ohira A, Swager TM (2007) Ordering of poly(p-phenylene ethynylene)s in liquid crystals. Macromolecules 40:19–25
10. Kukhta AV, Kukhta IN, Kolesnik EE, Lugovskii AP, Neyra OL, Meza E (2007) Optical properties of thiol terminated biphenyloxazole ordered monolayers on gold surface. Appl Surf Sci 254:116–119
11. Dudko EV, Kalosha II, Tolkachev VA (2005) Collisional quenching and depolarization of the fluorescence of the 2,5-diphenyloxazole and 2-phenylbenzoxazole vapors by oxygen. J Appl Spectrosc 72(1):43–48
12. Chaplanova ZhD, Mihailovski YuK, Agabekov VE, Olkhovik VK, Galinovskii NA, Gracheva EA (2007) Morphology and spectral properties of thin films of benzoxazole derivatives of biphenyl. J Appl Spectrosc 74(3):333–337
13. Jin Y, Kim J, Park SH, Lee K, Suh H (2005) Novel poly(p-phenylenevinylene)s derivatives with CF_3-phenyl substituent for light-emitting diodes. Bull Korean Chem Soc 26(5):795–801
14. Kim BJ, Park SY, Choi DH (2001) Effect of molecular aggregation on the photo-induced anisotropy in amorphous polymethacrylate bearing an aminonitroazobenzene moiety. Bull Korean Chem Soc 22:271–275
15. Frolov SV, Kloc Ch, Batlogg B, Wohlgenannt M, Jiang X, Vardeny ZV (2001) Excitation dynamics in single molecular crystals of α-hexathiophene from femtoseconds to milliseconds. Phys Rev B 63(20):205203
16. Bohn PW (1993) Aspects of structure and energy transport in artificial molecular assemblies. Ann Rev Phys Chem 44:37–60
17. Jenekhe SA, Yi Sh (2000) Efficient photovoltaic cells from semiconducting polymer heterojunctions. Appl Phys Lett 77 (17):2635–2637
18. Kukhta AV, Kolesnik EE, Kukhta IN, Olkhovik VK, Galinovskii NA, Agabekov VE, Kazakov SM, Andreev VA (2007) Electroluminescent properties of dibenzoxazolylbiphenyl molecules. J Appl Spectrosc 74(5):684–687